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Localized excitons in random and partly phase separated solid solutions: evidence of fractal structure of islands

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Abstract. Temperature dependence of photoluminescence (PL) spectra of MBE grown ZnSe/CdSe/ZnSe QWs with 0.3–1.5 ML nominal CdSe thicknesses as well as MOCVD grown double heterostructures (DHS) GaN/InGaN/GaN with In content in the range 0.004–0.06 within the temperature interval 2–300 K has been studied. Much in common has been found in the PL band temperature behavior for both systems. Depending on the concentration of the solid solution, the PL band maximum position $\epsilon_{\max}^{PL}(T)$ follows either "normal" or "anomalous" (known as "S-shape") dependence. We consider both dependences in detail and argue that anomalous behavior is caused by the fractal-like structure of the islands.

1. Experimental details and results

We have studied PL and excitation of PL (PLE) spectra of two systems: (i) single quantum wells formed by either MEE cycled deposition of CdSe (by 0.3 ML per cycle) in ZnSe matrices with the following number of cycles: 1, 2, 5, 8 and 10, or MBE grown ZnSe/CdSe/ZnSe QW with nominal CdSe content of 1.5 ML; and (ii) MOCVD grown GaN/InGaN/GaN double heterostructures with a well width and an In content ranging between 50–100 nm and 0.004 and 0.06, respectively (for more growth details see [1, 2]). The 441.6 nm or 325 nm He-Cd laser excitation were used for ZnCdSe and InGaN PL spectra, respectively. PLE spectra were excited by the second monochromator with a Xe-lamp. For both systems we have found that in the small composition range the PL spectra posses a fine structure, attributed to the exciton localization by clusters of 2 or 3 atoms of the narrow band component. It has been shown that the number of such clusters obeys the random distribution statistics [3, 4]. For Cd content in ZnCdSe more than $5 \cdot 0.3$ ML (which corresponds to $c = 0.15$ in the ZnCdSe QW [5]) as well as for In content exceeding ≈ 0.02 in InGaN solid solutions the PL fine structure is smoothed away and Stokes shifts between PL and PLE spectra is larger than that expected for the random statistics. Thus we can conclude that for more concentrated solid solutions the process of phase separation (or islands formation) starts to develop for the growth conditions used. In Figs. 1 and 2 temperature dependences of PL band maximum position $\epsilon_{\max}^{\mathrm{PL}}(T)$ of ZnCdSe and InGaN solid solutions, diluted (Figs. 1(a), 2(a)) and concentrated (Figs. 1(b,c) and 2(b,c)), respectively, are shown by symbols.

As it is seen in Figs. 1 and 2, for diluted solid solutions the maximum of PL band $\epsilon_{\max}^{\mathrm{PL}}(T)$ follows the temperature dependence which we shall call as "normal" for the reasons explained below: at the temperature increase $\epsilon_{\max}^{\mathrm{PL}}(T)$ shifts toward high energies and then tends to the band gap temperature dependence. At the increase of the narrow gap component

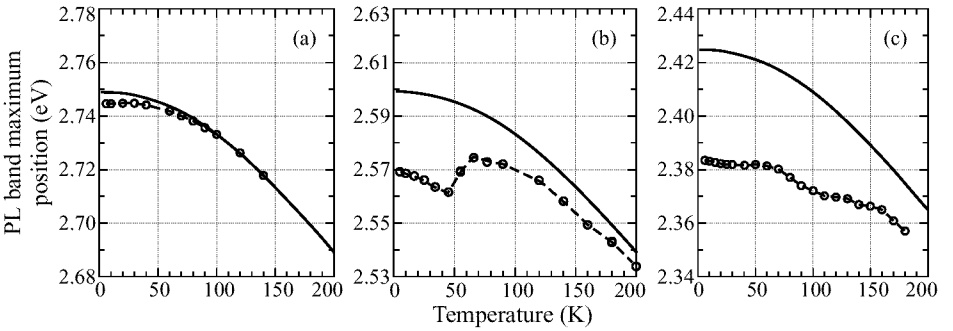

Fig. 1. PL band maximum versus the temperature (symbols) of ZnCdSe QWs with nominal Cd thicknesses 0.6 ML (a), 1.5 ML (b) and 2.4 ML (c). Solid lines — temperature dependence of corresponding PLE maximum.

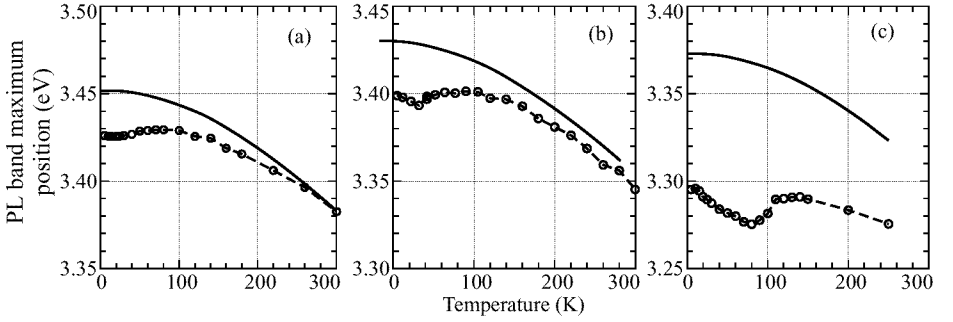

Fig. 2. Similar to that in Fig. 1 but for GaN/InGaN/GaN DHS with In content 0.005 (a), 0.02 (b) and 0.03 (c).

content, when the formation of nanoislands can be expected, the dependence of $\epsilon_{\max}^{\mathrm{PL}}(T)$ becomes "anomalous" (Figs. 1(b,c) and 2(b,c)): as the temperature raises, it shows either minor red shift, which is often wave-like modulated, or exhibits the distinct "S-shape" dependence with the pronounced red shift followed by blue shift and, afterwards, by the red shift again. Similar behavior was found also for more concentrated ZnCdSe QWs [5] and InGaN [7] solid solutions.

2. Discussion

2.1. Band gap temperature dependence

The band gap temperature dependence $E_g(T)$ results from the electron and hole interaction with lattice vibrations [8]. We have found that the dependence $E_g(T)$ for both ZnSe and GaN bulk materials can be well fitted by the sum of two terms proportional to the phonon occupation numbers: the first one with Debye temperature Θ_D of the host lattice and the second with $\Theta_{eff} \approx 0.2\Theta_D$, corresponding to the interaction with optical and acoustical phonons, respectively. In Figs 1 and 2 the obtained dependences for free exciton transitions of ZnSe ($\Theta_D = 340$ K [5]) and GaN ($\Theta_D = 570$ K [10]), shifted to fit the position of corresponding PLE maximum, are shown by solid lines. (For the solid solutions at low concentration the difference between Debye temperature of a wide-gap compound and that

of the solid solutions can be neglected). It is worth to note that the difference in the electron-phonon interaction of localized and free excitons can result in some difference in the thermal shift for localized excitons and in $E_g(T)$, but usually this difference is negligible.

2.2. Normal and anomalous temperature dependence of localized exciton PL band

Temperature shift of the localized exciton PL band maximum $\epsilon_{\max}^{\mathrm{PL}}(T)$ is determined by two causes: band gap dependence $E_g(T)$ and population of the excited states of super-clusters, which at low temperature relaxes nonradiatively to the ground states [4]. The latter factor leads to the blue shift of the PL band maximum until it reaches the position of the absorption band maximum. Then $\epsilon_{\max}^{\mathrm{PL}}(T)$ should follow $E_g(T)$ dependence. Such expected behavior completely agrees with the experimental behavior in the diluted solid solutions (see Figs. 1(a), 2(a)) and we regard this as a normal for random solutions. For more concentrated solutions, when the initial stage of phase separation takes place, the dependence $\epsilon_{\max}^{\mathrm{PL}}(T)$ essentially differs from the normal behavior.

2.3. Metastable electronic states of the island as a cause of anomalous dependence

The red shift of the PL maximum at low temperature indicates that an appreciable part of the radiative states of excitons in nanoislands are metastable rather than the ground ones and can relax to deeper ground states at the temperature increase, provided that at the lowest temperature the rate of nonradiative decay of these states is insufficient for the process to occur. One of the possible scenario of metastable state occurrence is formation of an archipelago consisting of a few slightly overlapping islands. The number of such archipelagos should be large enough to produce a pronounced effect on PL. For the statistical reasons a sufficient number of archipelagos can not arise occasionally as a result of random space distribution of islands due to small concentration of islands. Therefore, the complex archipelago-like islands should be an intrinsic feature of the island structure.

2.4. Diffusion-Limited Aggregations as an origin of metastable states

Some preliminary experiments indicate that thermal annealing of InGaN samples after the growth processes [11] or increasing a growth interruption time before the cap layer deposition in ZnSe/CdSe/ZnSe system [12] affects drastically the number and the composition of islands. These facts give evidence of an important role of the diffusion processes in island formation. Processes of diffusion limited aggregation lead to a complex shape of aggregates with disordered fractal properties ([13]). One of the important features of such aggregates is a multibranch structure with the common center. The most part of atoms are in branches, which are well isolated from each other by distances comparable with the size of branches. This assumption explains the observed PL band temperature dependence. Indeed, every branch of the aggregate can be treated as a separate island which is weakly connected with the others through center part of the fractal. Energy levels of the different branches are randomly distributed over some energy interval due to the random branch configuration. Localization of the exciton by different branches appears to have a comparable probability and the subsequent energy relaxation takes place if an occupied state is not the lowest one.

3. Summary

We have studied temperature dependences of the PL band maximum both in random and inhomogeneous solid solutions with partial phase separation. The arguments has been suggested that the anomalous temperature dependence reflects the fractal form of the islands caused by diffusion limited aggregation.

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